

CONTEMPORARY TRENDS IN THE SYNTHETIC ASPECTS, AND MAGNETIC PROPERTIES OF $3d-4f$ HETEROMETALLIC CUBANE, PARTIAL DICUBANE, AND PARTIAL TETRACUBANE CORE-TYPE COORDINATION COMPOUNDS

Abstract

Over the past two to three decades, the synthesis of multinuclear $3d-4f$ complexes acquired significant interest because of their fascinating topological structures, and intriguing properties in several areas, such as catalysis, magnetic materials, luminescent materials, and biomaterials. Compartmental ligands like Schiff bases are useful candidates in the manufacture of $3d-4f$ heterometallic multinuclear complexes as different coordination sites available for different metals. $4f$ ions like Eu(III), Dy(III), Tb(III), and Ho(III) are hard and oxophilic and preferentially interact with the oxygen-rich parts of ligands, while $3d$ ions like Mn(II/III), Fe(II), Ni(II), Cu(II) are soft in comparison and prefer nitrogen atoms for binding. Lanthanide (III) ions are regarded as potential building blocks for new types of magnetic materials due to their large magnetic anisotropy, which arises due to large spin-orbit coupling interactions. In this book chapter, we have discussed the synthetic aspects, and magnetic properties of $3d-4f$ coordination compounds with cubane, partial dicubane, and partial tetracubane cores.

Keywords: *Schiff base, Cubane, Partial Dicubane, Partial Tetracubane, Magnetic properties*

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I. INTRODUCTION

The preparation of 3d-4f mixed metal ion complexes has received enormous interest during the last three decades due to their fascinating structural topology and exciting magnetic properties for both potential and theoretical applications. [1, 2, 3, 4, 5] The first 3d-4f systems were discovered by Gatteschi et. al in 1985 and produced the first heterometallic Cu-Gd-Cu complex that showed ferromagnetic interactions. Some of the already reported 3d-4f systems with a variety of nuclearities are [Cu^{II}₄Ln^{III}], [Cu^{II}₄Ln^{III}], [Cu^{II}₉Ln^{III}], [Ni^{II}₈Ln^{III}]₆, [Ni^{II}₆Ln^{III}]₃, [Co^{II}₄Ln^{III}]₂, [Co^{II}₂Ln^{III}], [Co^{II}₂Ln^{III}]₄, [Mn^{II}₂Ln^{III}], [Fe^{III}₄Ln^{III}], etc. In addition to this, various 3d-4f systems have been discovered providing different structural topologies e.g. cage-like, cubane core-like, ring-like, and wheel-like structures. The formation of such a 3d-4f mixed metal complex is an extremely intricate process and it is regarded as an art. The selection of ligands is the most important aspect of the formation of intriguing structures. Multiple donor atoms should be present in ligands to bridge metal ions. 3d-4f mixed metal ions have precedence to associate with distinct donor atoms like nitrogen and oxygen, according to HSAB principle. For the preparation of 3d-4f mixed heterometallic complexes, two main methods are widely used from the standpoint of ligands: (1) design the ligands that can hold multiple coordination site for 3d as well as 4f metal ions; (2) introduction of suitable co-ligands that can support the self-assembly processes where both 4f ions and 3d metal ions can be coordinated with donor atoms in presence of multidentate ligands. The mentioned two synthetic processes to prepare such 3d-4f complexes are referred to as "assisted self-assembly", and "designed assembly" respectively. These sorts of multinuclear 3d-4f coordinate ion clusters exhibit Single Molecule Magnets (SMM) behavior.

The area of molecular magnetism has received some attention in current years owing to enormous progress in the synthesis followed by nanosized dodecanuclear [Mn₁₂] aggregate showing a bistable magnetic ground state (S=10 ground state) and magnetic hysteresis.[6, 7] Multinuclear complexes assembled by judiciously prepared ligands, 3d, and 4f metal ions are captivating candidates for magnetic molecular materials, with prodigious potential in the information storage device, spintronics, quantum computers, luminescence, and magnetocaloric materials. [8, 9, 10, 11] Among the all-lanthanide ions, Dy^{III}, Tb^{III}, Gd^{III}, Yb^{III}, and Ho^{III} ions show large magnetic anisotropy originating from unquenched spin-orbit coupling. The 4f metal ion containing compounds usually give decent performance as compared to 3d metal ion-based SMMs, the main reason for this is to the strong magnetic anisotropy of 4f metal ions. 4f metal ion-consisting systems also exhibit weak magnetic coupling interactions when it is attached in the ligand coordination pocket and bridge with one or more donor atoms. To boost the strength of magnetic coupling interactions as well as subduing of Quantum tunnelling of magnetization (QTM), significant synthetic approaches have been adopted for the building of a new generation of 3d-4f mixed heterometallic complexes. [12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22] The intriguing structure and wide range of uses of hybrid multinuclear complexes have prompted many researchers to seek out new and improved instances. Nonetheless, creating hetero-metallic compounds is a difficult undertaking. Chemists must devise synthetic techniques for combining various metal ions in a single unit while managing nuclearities, spin carrier topology, and dimensionality of the final compounds. Another difficult issue is to avoid the competition between different metal ions for the same or comparable coordination sites, which could lead to the creation of homo-

nuclear complexes or combinations of distinct species. In this book chapter, we have discussed the synthetic strategies and interesting magnetic properties of heterometallic 3d-4f complexes with Cubane, Partial Dicubane, and Partial Tetracubane core type geometries.

1. Syntheses and structural aspects of compounds containing Cubane cores : Debashis Ray et al. has recently synthesized five octanuclear Ni_4Ln_4 complexes $[\text{Ni}_4\text{Dy}_4(\text{HL1})_4(\mu_2\text{-OH})_2(\mu_3\text{-OH})_4(\mu\text{-OOCCH}_3)_8](\text{NO}_3)_2$ ($\text{Ln} = \text{Gd}$ (**1**), Tb (**2**), Dy (**3**), Ho (**4**), and Yb (**5**)) cubane type cores by reacting a phenol-based Schiff base ligand ($\text{H}_2\text{L1}$) 2-[(2-hydroxypropyl)imino]methyl]-6-methoxyphenol with $\text{Ln}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ salts, $\text{Ni}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ salt and LiOH (Figure 1) [23]. All the five complexes (**1**, **2**, **3**, **4**, **5**) were isostructural, with a difference only in the count of H_2O molecules that existed within the crystal lattice as demonstrated by the Single-crystal X-ray diffraction study. Among the five compounds, compounds **1**, **3**, and **4** crystallized with the $P\bar{1}$ triclinic space group ($Z = 1$), while compounds **2** and **5** crystallized with the $C2/m$ monoclinic space group ($Z = 2$). The Ni_2Dy_2 cubic core belonging to the asymmetric unit of complex **3** was constructed by two Ni^{II} ions, two Dy^{III} ions, two HL^- from the ligand, three HO^- groups, and four acetate (AcO^-) ions. Further, these two Ni_2Dy_2 cubic cores are connected by four acetate ions clips and two HO^- groups to develop a double cubane Ni_4Dy_4 structure. The tridentate pocket (ONO) of the ligand HL^- coordinated with one Ni^{II} center meridionally and an adjoining bidentate (OO) pocket of the ligand was utilized to trap oxophilic Ln^{III} ion. [23] In the Ni_4Dy_4 complex, Dy_1^{III} and Dy_2^{III} prevailed in the distorted trigonal dodecahedral coordination environment, and Ni^{II} ions existed in a distorted octahedral coordination geometry around the center.

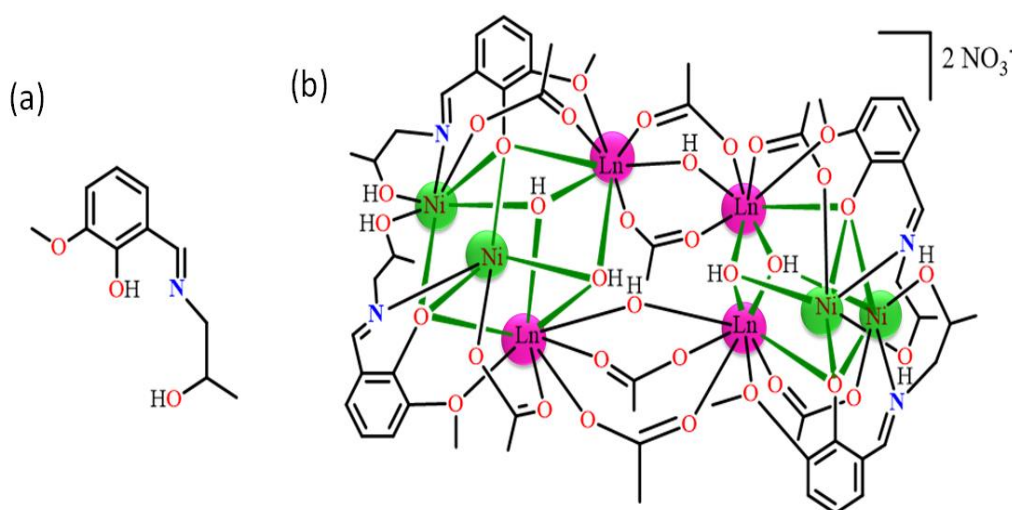


Figure 1: (a) Schiff base ligand $\text{H}_2\text{L1}$ structure. (b) View of Ni_4Ln_4 complexes ($\text{Ln} = \text{Gd}$ (**1**), Tb (**2**), Dy (**3**), Ho (**4**), and Yb (**5**)) with cubane cores. Reference 23. Copyright 2020 Wiley.

His, other work, reported four tetranuclear heterometallic Ni-Ln complexes $[\text{Ni}^{\text{II}}_2\text{Ln}^{\text{III}}_2(\mu_3\text{-L2})_2(\mu_3\text{-OH})_2(\mu\text{-OAc})_3(\text{AcO})(\text{H}_2\text{O})_3]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ ($\text{Ln} = \text{Gd}$, **6**; Tb , **7**; Dy , **8**; Ho , **9**) with cubane type cores by the reaction of 1-(2-hydroxy-3-methoxybenzylidene)semicarbazide (HL2) in presence of triethyl amine and sodium

acetate [24]. The single crystal X-ray diffraction study of compounds (**6-9**) disclosed that all the complexes crystallized using monoclinic crystal system with $P2_1/n$ space group ($Z = 4$) (Figure 2). The authors have chosen Ni_2Tb_2 complex (**7**) as a representative for detailed structural discussions. The tetranuclear $Ni_2Tb_2O_4$ hetero-cubane core was constructed by the two μ_3 - PhO^- (O1 and O2) fragments of the ligand ($L2^-$) and the two μ_3 - HO^- (O3 and O4) groups which were generated from water molecules and three μ -O, O'-acetato. The $\mu_{1,3}$ - AcO^- bridges in three faces (two $Ni \cdots Tb$ and one $Tb \cdots Tb$) of the cube supported the aggregation process. Nickel (II) ion present in all the structures showed distorted octahedral geometry in the NO_5 coordination environment. The Tb1 and Tb2 present in the structure existed as coordination number 8, where Tb1 displayed distorted triangular dodecahedron geometry, but Tb2 exhibited distorted square antiprismatic geometry. The eight coordination sites of Tb^{III} are fulfilled by the bidentate coordination (OO donor) from $L2^-$, two hydroxide and acetato bridges, and two terminal monodentate coordination from H_2O molecules for Tb2 center, one monodentate coordination from H_2O molecules and one AcO^- molecules to the Tb1 center [24].

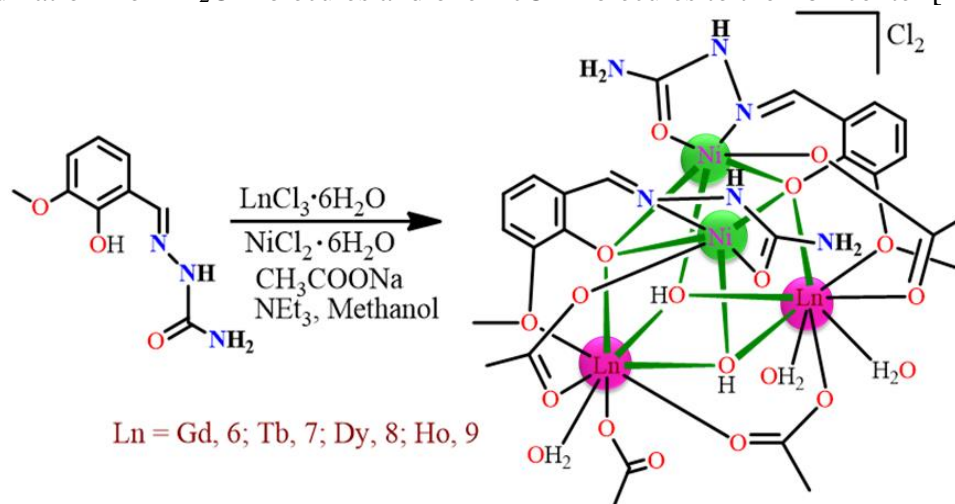


Figure 2: (a) Synthetic pathway for the preparation of tetranuclear Ni-Ln complexes (Ln = Gd, **6; Tb, **7**; Dy, **8**; Ho, **9**) from ligand HL2. Reference 24. Copyright 2020 Royal Society of Chemistry.**

A work executed by Zhiliang Liu et al., has reported three novel heterometallic Ln_2Ni_2 clusters $[Ln_2Ni_2(\mu_3-OH)_2(OH)(OAc)_4(HL3)_2(MeOH)_3(ClO_4) \cdot 3MeOH]$ [$Ln = Dy$ (**10**), Tb (**11**), and Gd (**12**)] representing a new 3d-4f heterometallic motif with cubane type core. [25] These complexes were synthesized by the reaction of $Ln(ClO_4)_3 \cdot nH_2O$ salts ($Ln = Dy$ (**10**), Tb (**11**), and Gd (**12**)), $Ni(OAc)_2 \cdot H_2O$, and 2-(benzothiazol-2-ylhydrazonomethyl)-6-methoxyphenol ligand (H_2L3) in presence of $NaOH$ (Figure 3). Single-crystal X-ray diffraction (SCXRD) study divulged that all the complexes (**10-12**) were isostructural, and the central core possesses $[Ln_2Ni_2O_4]$ cubane core. All three complexes (**10, 11, 12**) crystallized in $Pna2_1$ orthorhombic space group. Tb_2Ni_2 complex (**11**) was taken as a representative example. The tetranuclear metal centers in the Tb_2Ni_2 complex (**11**) were linked with two μ_3 -phenoxido oxygen atoms along with two μ_3 - OH^- groups from two $HL3^-$ ligands resulting in a cubic arrangement of the metal ions. The N, N, and O, O pockets present in the ligand coordinated with Ni^{II} and Tb^{III} metal ion in an

anti-parallel fashion, it was further bridged with acetates in μ - η^1 : η^1 fashion to construct heterometallic cubane. The Tb1 and Tb2 center in the complex formed dodecahedral and bicapped trigonal prismatic geometry having an eight-coordinate number. On the other hand, the Ni^{II} ion present in the complex showed distorted octahedral geometry. The basal plane of the octahedron consisted of one bridging phenoxido (PhO⁻) oxygen atom and two nitrogen atoms belonging to one HL3⁻ ligand and the fourth coordination site was fulfilled by one oxygen atom from a bridging OH⁻ group. The apical positions were occupied by two oxygen atoms, one was from the OAc⁻ group and another one was from the phenoxido (PhO⁻) oxygen atom of a second HL3⁻ ligand (Figure 3).

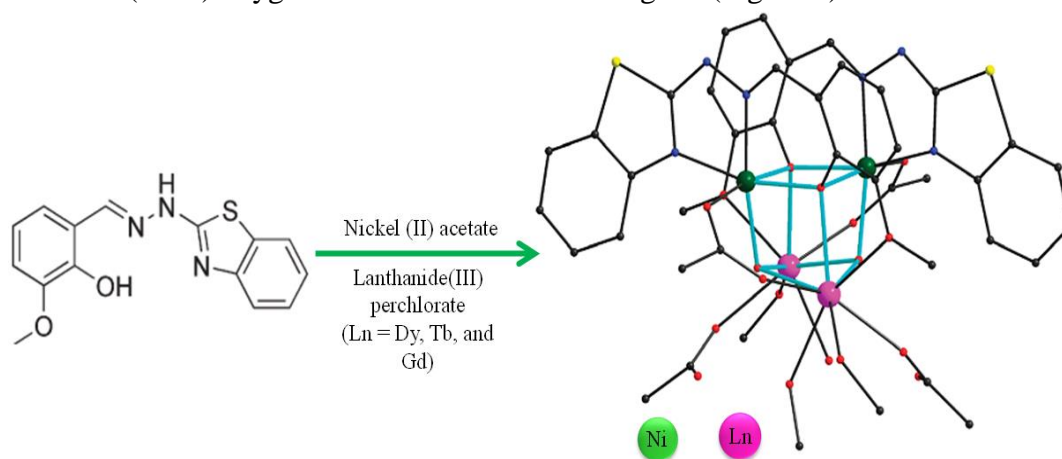


Figure 3: (a) Synthetic pathway for the preparation of heterometallic Ln₂Ni₂ [Ln = Dy (10), Tb (11), and Gd (12)] complexes. Reprinted with permission from reference 25. Copyright 2011 American Chemical Society.

3. Syntheses and structural analyses of compounds containing partial dicubane cores :

Ray and co-workers have established a family of four Ni-Ln isostructural butterfly-shaped partial dicubane core complexes [Ln₂Ni₂(L₄)₂(μ ₃-OCH₃)₂(μ _{1,3}-PhCO₂)₂(PhCO₂)₂(CH₃OH)₄·2CH₃OH [where Ln=Gd (13), Tb (14), Dy (15) and Ho (16)]. [26] The four complexes have been prepared by the reaction of 2-[(2-hydroxybenzyl)imino]methyl-6-methoxyphenol ligand (H₂L₄) with Ni(NO₃)₂·6H₂O and Ln(NO₃)₃·xH₂O salts [Ln= Gd (13), Tb (14), Dy (15) and Ho (16)] in presence of sodium benzoate as co-ligand and triethylamine as the base (Figure 4a). The Single-crystal X-ray diffraction study (SCXRD) established that all the four complexes (13, 14, 15, and 16) consisted of partial dicubane core (Figure 4b). The Ni₂Ln₂O₆ butterfly-shaped partial dicubane core of each complex was supported by two (L₄²⁻) ligand anions and two μ ₃-OCH₃ groups. The Ni^{II} metal ion showed distorted octahedral geometry in all the complexes with coordination from two oxygen (O) atoms of ligand (L₄²⁻), two O of two μ ₃-OCH₃ groups of MeOH, and one O from one benzoate group. Whereas Ln^{III} ion showed distorted trigonal dodecahedral geometry with eight coordination by three oxygen atoms from two L₄²⁻ ligands, one oxygen atom from the μ ₃-OCH₃ group, two oxygen from the -PhCO₂ moiety, and two oxygen from MeOH solvent molecule.

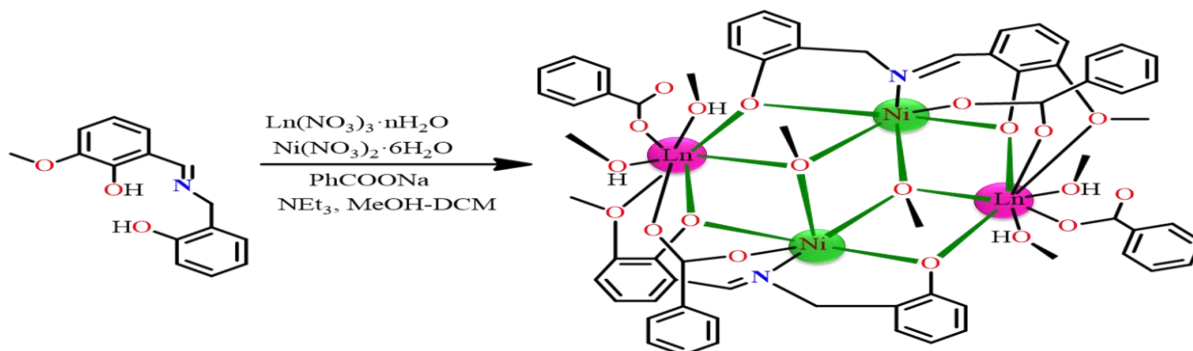


Figure 4: (a) Synthetic pathway for the preparation of Ni-Ln complexes where Ln= Gd (13), Tb (14), Dy (15) and Ho (16). Reference 26. Copyright 2021 Royal Society of Chemistry.

4. Syntheses and structural aspects of compounds containing Partial Tetracubane cores;

In another work, Debashis Ray et.al synthesized N_2O_4S donor atoms containing Schiff base ligand (H_2L5) [2-((2-(2-(2-hydroxy-3-methoxybenzylideneamino)ethylthio)ethylimino) methyl)-6-methoxyphenol]] and also explored its capability to give 3d-4f metal complexes (Figure 5a). The Schiff base ligand H_2L5 was treated with triethyl amine (Et_3N), $Ln(NO_3)_3 \cdot 5H_2O$ and $NiCl_2 \cdot 6H_2O$ in MeCN–MeOH (2:1) mixed solvent at room temperature and generated three complexes of formula $[Ni_4Ln_2(L5)_2(\mu-Cl)_2(\mu_3-OH)_4(H_2O)_6]Cl_4 \cdot 2H_2O$, where $Ln = Dy^{3+}$ (**17**), Tb^{3+} (**18**) and Ho^{3+} (**19**), which are having Partial Tetracubane cores (Figure 5b). [27] The authors also prepared $[Ni_4Ln_2(L5)_2(\mu-NCS)_2(\mu_3-OH)_4(NCS)_4(H_2O)_2] \cdot xMeOH \cdot yH_2O$ (where $Ln = Dy^{3+}$ (**20**), $x = 2$, $y = 4$; Tb^{3+} (**21**) and Ho^{3+} (**22**), $x = 0$, $y = 14.1$) complexes **20**, **21** and **22** using the same Schiff base ligand H_2L5 and $Ni(SCN)_2 \cdot 4H_2O$ (Figure 5c). The SCXRD study divulged that all the six (**17-22**) complexes acquired defective hexanuclear tetracubane cores. Complex **17**, **18**, and **19** all are isostructural and all the complexes possessed $P2_1/n$ monoclinic space group whereas Complex **20** and **21** displayed $P\bar{1}$ triclinic space group, and complex **22** crystallized in the monoclinic crystal system with $C2/c$ space group. The crystal structure of complex **17**, which was taken as a representative among **17**, **18**, and **19**, has revealed that in pockets I each $L5^{2-}$ unit binds with two Ni^{II} centers whereas in pocket II asymmetric coordination of two 3d ions was observed

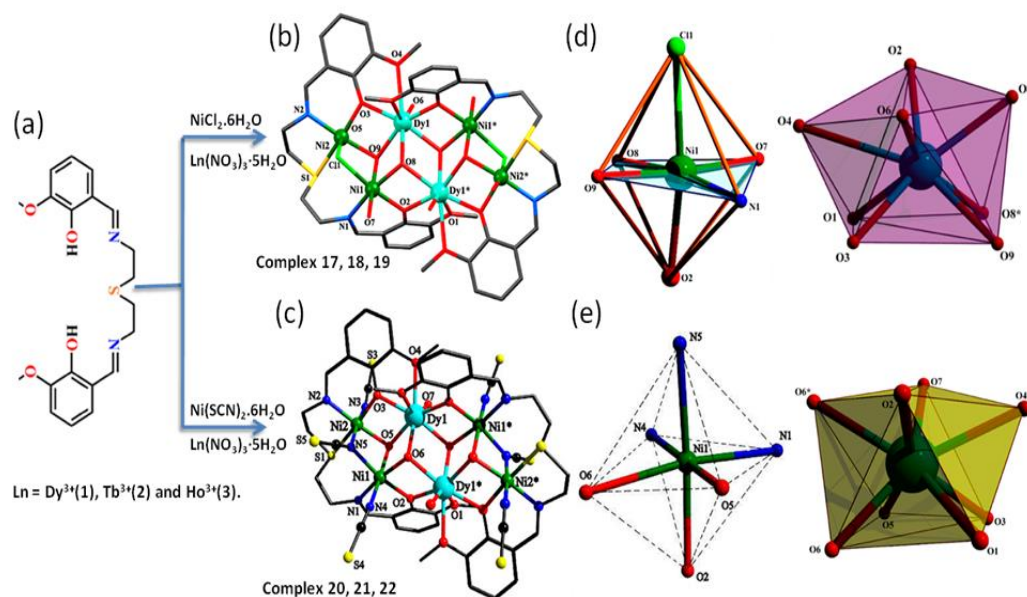


Figure 5: (a) Structure of Schiff base ligand H₂L5. (b) View of crystal structures of 17, 18, and 19 with the partial atom numbering scheme. (c) Molecular structure of 20, 21, and 22. (d) Distorted octahedral coordination environment about both the Ni(II) centers, and distorted triangular dodecahedron coordination environment around the Dy(III) centers in 17, 18, and 19. (e) Distorted octahedral coordination geometry about the Ni(II) ions, and Distorted trigonal dodecahedral coordination geometry about the Dy(III) ions in 20, 21, and 22. Reprinted with permission from reference 27. Copyright 2019 American Chemical Society.

The pockets III and IV of the ligands were used to bind oxophilic Dy^{III} ions through the O, O donor part of the ligand. The hexanuclear centrosymmetric Ni^{II}₄Ln^{III}₂ was formed by endogenous four μ -O^{Ph} groups and four exogenous μ_3 -OH groups of four defective cubanes. On the other hand, the crystal structure of complex 20, 21, and 22 showed that all the three complexes are electro-neutral as the terminal water molecules were replaced by NCS⁻ ions which were bound to the Ni^{II} centers. In all the complexes (17-22) Ni(II) ions formed distorted octahedral coordination geometry but the Ln(III) ions present in complexes (17,18, 19) formed distorted triangular dodecahedron coordination geometry (Figure 5d), and in complexes (20, 21, 22) displayed distorted trigonal dodecahedral geometry (Figure 5e).

Jinkui Tang et.al. have also reported a new family of hexanuclear complexes, [Ni₄M₂(μ_3 -OH)₂(L6)₄(OAc)₂(NO₃)₂(H₂O)₂·kC₂H₅OH·mCH₃OH·nH₂O [M = Gd^{III} with k = 5 and n =1(23), Dy^{III} with k = 4 and n =2(24), and Y^{III} with k = 5 and m =1(25)] with partial tetracubane cores (Figure 6a). All three complexes were produced by using lanthanide(III) nitrate, nickel(II) acetate, and triethyl amine with 2-(2-hydroxy-3-methoxybenzylideneamino)Schiff-base ligand (H₂L6). All three complexes (23-25) have similar core structures with only a difference in the solvent of crystallization. The SCXRD studies disclosed that complexes 23, 24 crystallized in the monoclinic crystal system with C2/c space group, while complex 25 was found in $P\bar{1}$ triclinic space group.

Each Ni_2DyO_4 subunit comprised of one Dy(III) centre and two Ni(II) centres organized as a defective cubane with one missing vertex. Two phenoxido groups connected one Dy(III) ion and one Ni(II) ion by doubly bridged mode, whereas the other one connected three Ni(II) ions with triply bridged binding mode (Figure 6b). The Ni(II) ions present in all three compounds are hexa-coordinated distorted octahedral geometry with the NO_5 environment. Each Lanthanide ion is connected through phenoxido groups and the hydroxido group of the ligand towards the central Ni(II) ions which provided Ni_2DyO_4 defective cubane core. [28]

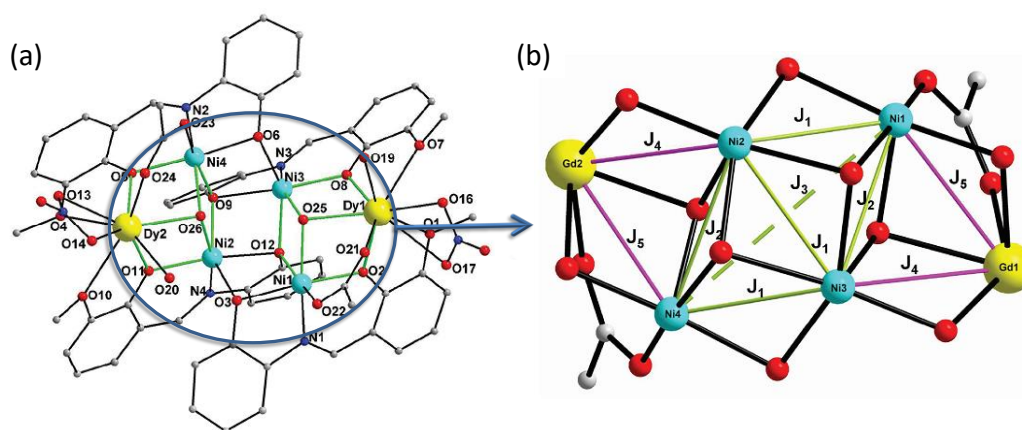


Figure 6: (a) Structure of the H_2L_6 Ligand. (b) View of complex 24 showing the $[\text{Ni}_2\text{GdO}_4]$ heterometallic defective cubane core. Reprinted with permission from reference 28. Copyright 2012 American Chemical Society.

5. Magnetic analyses of compounds containing cubane cores: The variable temperature magnetic study of the octanuclear Ni-Ln complexes **1-5** revealed ferromagnetic coupling interaction between the existing metal ions [23]. Further, frequency-dependent AC susceptibility measurements with no applied dc field displayed tails of an out-of-phase peak down to 2 K for Tb(III) (**2**) and Dy(III) (**3**) containing compounds. These results indicated that among all the five complexes, Tb(III) and Dy(III) were the most anisotropic lanthanide ions which showed SMM behavior [23].

Magnetic properties of tetranuclear heterometallic Ni-Ln complexes **6-9** revealed that despite showing large ground state magnetic moment values, all of them did not show any SMM behaviour. This observation was also justified as out-of-phase ac susceptibility signals were not observed in any of the complexes [24].

The magnetic study of complex **10** revealed slow magnetic relaxation with frequency-dependent out-of-phase signal in AC susceptibility measurements. Whereas, in the DC field it was significantly slowed down which was generally showing up the presence of fast zero-field relaxation of magnetization. Complex **12** indicated ferromagnetic exchange interactions among $\text{Gd}\cdots\text{Ni}$ competing with $\text{Ni}\cdots\text{Ni}$ anti-ferromagnetic interactions [25].

- 7. Magnetic analyses of compounds containing Partial Dicubane cores:** DC magnetic analysis study of the complexes **13**, **14**, **15** and **16**, supported by DFT and CASSCF calculations showed dominating ferromagnetic exchange interactions between Ni–Ni ions ($J_{\text{Ni-Ni}} = 7.16 \text{ cm}^{-1}$), and also in between *3d-4f* ions ($J_{\text{Gd-Ni}} = 0.715 \text{ cm}^{-1}$, $J_{\text{Tb-Ni}} = 1.25 \text{ cm}^{-1}$, $J_{\text{Dy-Ni}} = 0.873 \text{ cm}^{-1}$, and $J_{\text{Ho-Ni}} = 1.42 \text{ cm}^{-1}$). An AC magnetic analysis study revealed that no slow relaxation was observed i.e., the complexes lack SMM characteristics [26].
- 8. Magnetic analyses of compounds containing Partial Tetracubane cores:** AC susceptibility data complexes **20**, **21** **22** revealed an out-of-phase nonzero signal at zero static magnetic field, which confirmed the presence of slow magnetic relaxation for SMMs. Both Ni_4Dy_2 (**17** and **20**) and Ni_4Tb_2 (**18** and **21**) complexes showed frequency-dependent maxima in the AC susceptibility (χ'') measurement. So, at zero static field complexes **17**, **18** **19**, and **20** behave as SMMs which was rare in other reports [27].

The magnetic study of **23**, **24**, and **25** revealed that compound **23** ($M = \text{Gd}$) displayed a combination of ferromagnetic and antiferromagnetic coupling pathways with the absence of SMM behaviors. Whereas, in compound **24**, Dy(III) ions in the core lead to slow magnetic relaxation, which was further established by frequency-dependent out-of-phase ac signal. The magnetic properties of compound **25** indicated anti-ferromagnetic Ni...Ni exchange interactions contending with ferromagnetic exchange interactions, which are mediated by the Ni–O–Ni bridging angles [28].

II. CONCLUSION

In the recent past, the chemistry of heterometallic *3d-4f* compounds has augmented rapidly due to the state-of-the-art technology available for the characterizations of the prepared compounds. Among the characterization techniques, single crystal X-ray diffraction is widely used for structure determination, and the low-temperature SQUID instrument is used for magnetic measurement studies. However, concerning the development of more such *3d-4f* compounds with optimized reaction pathways and also understanding the both computational and experimental magnetic exchange interactions between the *3d* and *4f* metal ions still requires a lot of effort. The incorporation of high anisotropic *4f* Ln(III) ions with *3d* ions enhance the possibility to achieve slow magnetization relaxation which is essential for SMM property. In summary, in this book chapter, intending to enhance the *3d-4f* systems database we have reported some recent literature reports of *3d-4f* coordination compounds with cubane, partial dicubane, and partial tetracubane cores focusing on their synthetic aspects, and magnetic interactions.

Conflicts of interest: The authors declare no competing financial interest.

Acknowledgments: The authors acknowledge the Department of Chemistry, ICFAI University Tripura. B. C. R. acknowledges ICFAI University Tripura for the fellowship.

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